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CLAIMS

1. A modification method of the surface layer of a molded resin article which comprises the steps of:

5 placing, in a closed space, an organic compound having sublimation properties and an affinity for a resin of a molded resin article to be coated, and the molded resin article;

10 bringing the closed space to a saturated sublimation pressure state of the organic compound;

15 uniformly depositing a vapor of the organic compound on the surface of the molded resin article; and

20 allowing the deposited organic compound to penetrate/disperse from the surface of the molded resin article into its inside.

25 2. A modification method of the surface layer of a molded resin article which comprises the steps of:

30 placing, in a first closed space, an organic compound having sublimation properties and an affinity for a resin of a molded resin article to be coated;

35 on the other hand, placing the molded resin article in a second closed space;

40 controlling a temperature in the second closed space so as to be equal to or higher than the temperature in the first closed space;

45 bringing a pressure in the first closed space to a saturated sublimation pressure state of the organic compound;

50 controlling a pressure in the second closed space so as to be equal to or lower than the pressure in the first closed space;

subsequently, connecting the first closed space to the second closed space to form a third closed space in which the first closed space is combined with the second closed space, and further controlling the temperature and the pressure so that the whole of the third closed space may be in the saturated
5 sublimation pressure state of the organic compound;

allowing a vapor of the organic compound with which the first closed space before the connection is filled to diffuse into the second closed space before the connection;

10 uniformly depositing the vapor of the organic compound on the surface of the molded resin article; and

allowing the deposited organic compound to penetrate/disperse from the surface of the molded resin article into its inside.

15 3. The modification method of the surface layer of the molded resin article according to claim 1 wherein:

the organic compound is deposited on or contained in a sublimation source substrate in at least one manner selected from the group consisting of the following five manners (A) to (E) so that the organic compound can be deposited on the surface of the molded resin article:

20 (A) the organic compound being singly applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

(B) the organic compound and a binder resin being applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

25 (C) a porous particle impregnated with the organic compound being applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

(D) the porous particle impregnated with the organic compound and the binder resin being applied onto the surface of the sublimation source substrate, or formed into a film on the surface; and
5 (E) a hole in the surface of a porous sublimation source substrate being impregnated with the organic compound.

4. The modification method of the resin surface layer according to claim 3 wherein:

10 the surface of the sublimation source substrate, on or in which the organic compound is deposited or contained in any one manner of said manners (A) to (E), is disposed in the vicinity of the surface of the molded resin article.

15 5. The modification method of the resin surface layer according to claim 1 which comprises the steps of:

placing the molded resin article and the organic compound in a vacuum container;

20 exhausting air through a vacuum valve disposed in the vacuum container to reduce the pressure in the vacuum container to a saturated sublimation pressure of the organic compound at a temperature which is equal to or higher than room temperature and which does not exceed a thermal decomposition temperature of the organic compound and/or the resin;

tightly closing all the vacuum valves disposed in the vacuum container to form a closed space;

25 raising the temperature in the tightly closed vacuum container up to a temperature at which a partial pressure of the organic compound reaches the saturated sublimation pressure in the reduced pressure state; and

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after the heating for a predetermined time, slowly cooling the vacuum container.

6. The modification method of the resin surface layer according to
5 claim 3 which comprises the steps of:

placing, in a vacuum container, the organic compound deposited on or contained in the sublimation source substrate in any one manner of the manners according to claim 3, and the molded resin article;

10 exhausting air through a vacuum valve disposed in the vacuum container to reduce the pressure in the vacuum container to a saturated sublimation pressure of the organic compound at a temperature which is equal to or higher than room temperature and which does not exceed a thermal decomposition temperature of the organic compound and/or the resin;

15 tightly closing all the vacuum valves disposed in the vacuum container to form a closed space;

raising the temperature in the tightly closed vacuum container up to a temperature at which a partial pressure of the organic compound reaches the saturated sublimation pressure in the reduced pressure state; and

20 after the heating for a predetermined time, slowly cooling the vacuum container.

7. The modification method of the resin surface layer according to
claim 4 which comprises the steps of:

25 placing, in a vacuum container, the organic compound deposited on or contained in the sublimation source substrate in any one manner of the manners according to claim 3, and the molded resin article;

exhausting air through a vacuum valve disposed in the vacuum

container to reduce the pressure in the vacuum container to a saturated sublimation pressure of the organic compound at a temperature which is equal to or higher than room temperature and which does not exceed a thermal decomposition temperature of the organic compound and/or the resin;

5 tightly closing all the vacuum valves disposed in the vacuum container to form a closed space;

raising the temperature in the tightly closed vacuum container up to a temperature at which a partial pressure of the organic compound reaches the saturated sublimation pressure in the reduced pressure state; and

10 after the heating for a predetermined time, slowly cooling the vacuum container.

8. The modification method of the resin surface layer according to claim 1 which comprises the steps of:

15 placing the molded resin article and the organic compound in a vacuum container;

raising the temperature in the vacuum container up to a temperature which is equal to or higher than room temperature and which does not exceed a thermal decomposition temperature of the organic compound and/or the resin;

20 while keeping the above temperature, exhausting air through a vacuum valve disposed in the vacuum container to reduce the pressure in the vacuum container to a saturated sublimation pressure of the organic compound at the above temperature;

25 tightly closing all the vacuum valves disposed in the vacuum container to form a closed space; and

 after the heating and the pressure reduction for a predetermined

time, slowly cooling the vacuum container.

9. The modification method of the resin surface layer according to claim 3 which comprises the steps of:

5 placing, in a vacuum container, the organic compound deposited on or contained in the sublimation source substrate in any one manner of the manners according to claim 3, and the molded resin article;

10 raising the temperature in the vacuum container up to a temperature which is equal to or higher than room temperature and which does not exceed a thermal decomposition temperature of the organic compound and/or the resin;

15 while keeping the above temperature, exhausting air through a vacuum valve disposed in the vacuum container to reduce the pressure in the vacuum container to a saturated sublimation pressure of the organic compound at the above temperature;

tightly closing all the vacuum valves disposed in the vacuum container to form a closed space; and

after the heating and the pressure reduction for a predetermined time, slowly cooling the vacuum container.

20 10. The modification method of the resin surface layer according to claim 4 which comprises the steps of:

25 placing, in a vacuum container, the organic compound deposited on or contained in the sublimation source substrate in any one manner of the manners according to claim 3, and the molded resin article;

raising the temperature in the vacuum container up to a temperature which is equal to or higher than room temperature and which

does not exceed a thermal decomposition temperature of the organic compound and/or the resin;

while keeping the above temperature, exhausting air through a vacuum valve disposed in the vacuum container to reduce the pressure in the vacuum container to a saturated sublimation pressure of the organic compound at the above temperature;

5 tightly closing all the vacuum valves disposed in the vacuum container to form a closed space; and

10 after the heating and the pressure reduction for a predetermined time, slowly cooling the vacuum container.

11. The modification method of the resin surface layer according to claim 2 which comprises the steps of:

15 placing the organic compound having the sublimation properties and the affinity for the resin of the molded resin article to be coated in a first vacuum container provided with a pipe to an exhaust system, an introducing portion of the organic compound and a connection pipe to a second vacuum container, closing the organic compound introducing portion and the connection pipe to the second vacuum container, reducing the pressure in the first vacuum container through the exhaust system to a saturated 20 sublimation pressure of the organic compound at a temperature which is equal to or higher than room temperature and which does not exceed a thermal decomposition temperature of the organic compound and/or the resin, and raising the temperature in the first vacuum container up to the above 25 temperature;

on the other hand, placing the molded resin article in the second vacuum container provided with a pipe to an exhaust system, an introducing

portion of the molded resin article and a connection pipe to the first vacuum container, and closing the molded resin article introducing portion and the connection pipe to the first vacuum container;

5 controlling the temperature in the second vacuum container so as to be equal to or higher than the temperature in the first vacuum container;

bringing the pressure in the first vacuum container to a saturated sublimation pressure state of the organic compound;

controlling the pressure in the second vacuum container so as to be equal to or lower than the pressure in the first vacuum container;

10 subsequently, connecting the first vacuum container to the second vacuum container via a mutual connection pipe to form the third closed space in which the first closed space in the first vacuum container is combined with the second closed space in the second vacuum container, and further controlling the temperature and the pressure so that the whole of the third closed space may be in the saturated sublimation pressure state of the organic compound;

allowing the vapor of the organic compound with which the first vacuum container before the connection is filled to diffuse into the second vacuum container before the connection;

20 uniformly depositing the vapor of the organic compound on the surface of the molded resin article;

heating for a predetermined time to allow the deposited organic compound to penetrate/disperse from the surface of the molded resin article into its inside;

25 closing the connection pipe which connects the first vacuum container to the second vacuum container;

controlling the temperature and the pressure in the second vacuum

container for a predetermined time so that the vapor of the organic compound which remains inside the second vacuum container may penetrate/disperse from the surface of the molded resin article into its inside;

5 when the vapor of the organic compound excessively exists in the second vacuum container, exhausting the vapor of the organic compound from the second vacuum container through the exhaust system; and

then returning the temperature of the molded resin article in the second vacuum container to ordinary temperature.

10 12. The modification method of the resin surface layer according to claim 11 wherein:

instead of returning the temperature of the molded resin article in the second vacuum container to ordinary temperature in a final stage,

15 the molded resin article is transported under a reduced pressure into a third vacuum container which is disposed adjacent to the second vacuum container via a gate valve and in which the pressure can independently be controlled, and the temperature of the molded resin article is then returned to ordinary temperature.

20 ~~13. The modification method of the resin surface layer according to any one of claims 5, 6, 7, 8, 9, 10, 11 and 12 wherein:~~

the vapor of the organic compound is uniformly deposited on the surface of the molded resin article; and

25 in order to allow the deposited organic compound to penetrate/disperse from the surface of the molded resin article into its inside,

the temperature of the molded resin article is raised up to a temperature which is equal to or higher than a glass transition temperature

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~~of the resin and which does not exceed the thermal decomposition temperature of the organic compound and/or the resin.~~

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14. The modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 wherein:

a dyestuff having the sublimation properties and the affinity for the resin of the molded resin article to be coated is used as the organic compound to modify and simultaneously color the surface layer of the molded resin article.

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15. The modification method of the resin surface layer according to claim 13 wherein:

a dyestuff having the sublimation properties and the affinity for the resin of the molded resin article to be coated is used as the organic compound to modify and simultaneously color the surface layer of the molded resin article.

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16. A modification apparatus for the surface layer of a resin which comprises:

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a tightly closable container for placing an organic compound having sublimation properties and an affinity for a resin of a molded resin article to be coated, and the molded resin article in a saturated sublimation pressure state of the organic compound;

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an exhaust system for adjusting a pressure in the tightly closable container; and

heating means for allowing the organic compound to penetrate/disperse into the molded resin article, after the organic compound

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sublimes and a vapor of the organic compound is deposited on the surface of the molded resin article.

17. The modification apparatus for the surface layer of the molded resin article according to claim 16 which further contains:

a sublimation source substrate on which the organic compound is held in at least one manner selected from the group consisting of the following five manners (A) to (E) so that the organic compound can be deposited on the surface of the molded resin article:

(A) the organic compound being singly applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

(B) the organic compound and a binder resin being applied onto the surface of the sublimation source substrate, or formed into the film on the surface;

(C) a porous particle impregnated with the organic compound being applied onto the surface of the sublimation source substrate, or formed into the film on the surface;

(D) the porous particle impregnated with the organic compound and a binder resin being applied onto the surface of the sublimation source substrate, or formed into the film on the surface; and

(E) a hole in the surface of a porous sublimation source substrate being impregnated with the organic compound.

18. A modification apparatus for a resin surface layer which comprises:

a tightly closable first vacuum container for placing an organic compound having sublimation properties and an affinity for a resin of a

molded resin article to be coated in a saturated sublimation pressure state;

a tightly closable second vacuum container for placing the molded resin article in the saturated sublimation pressure state of the organic compound;

5 a connection pipe for connecting the first vacuum container to the second vacuum container;

an opening/closing mechanism of the connection pipe;

an exhaust system for independently adjusting the pressure in the first vacuum container;

10 an exhaust system for independently adjusting a pressure in the second vacuum container; and

heating means for allowing the organic compound to penetrate/disperse into the molded resin article, after the organic compound sublimes and a vapor of the organic compound is deposited on the surface of the molded resin article.

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19. The modification apparatus for the resin surface layer according to any one of claims 16, 17 and 18 which further contains:

a stirring mechanism for stirring the molded resin article of a powder form.

20. The modification apparatus for the resin surface layer according to any one of claims 16, 17 and 18 which further contains:

a wind-up mechanism for winding up the molded resin article of a form selected from a textile form, a fiber form and a film form around a reception side reel from a supply side reel under reduced pressure.

21. A coloring apparatus for the surface layer of a molded resin article which comprises:

a tightly closable container for placing a dyestuff having sublimation properties and an affinity for a resin of a molded resin article to be colored, and the molded resin article in a saturated sublimation pressure state of the dyestuff;

an exhaust system for adjusting a pressure in the tightly closable container; and

heating means for allowing the dyestuff to penetrate/disperse into the molded resin article, after the dyestuff sublimes and a vapor of the dyestuff is deposited on the surface of the molded resin article.

22. The coloring apparatus for the surface layer of the molded resin article according to claim 21 which further contains:

a sublimation source substrate on which the dyestuff is held in at least one manner selected from the group consisting of the following five manners (A) to (E) so that the dyestuff can be deposited on the surface of the molded resin article:

(A) the organic compound being singly applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

(B) the organic compound and a binder resin being applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

(C) a porous particle impregnated with the organic compound being applied onto the surface of the sublimation source substrate, or formed into a film on the surface;

(D) the porous particle impregnated with the organic compound

and the binder resin being applied onto the surface of the sublimation source substrate, or formed into a film on the surface; and

(E) a hole in the surface of a porous sublimation source substrate being impregnated with the organic compound.

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23. A coloring apparatus for a resin surface layer which comprises:
a tightly closable first vacuum container for placing a dyestuff having sublimation properties and an affinity for a resin of a molded resin article to be colored in a saturated sublimation pressure state;

10 a tightly closable second vacuum container for placing the molded resin article in the saturated sublimation pressure state of the dyestuff;

a connection pipe for connecting the first vacuum container to the second vacuum container;

an opening/closing mechanism of the connection pipe;

15 an exhaust system for independently adjusting the pressure in the first vacuum container;

an exhaust system for independently adjusting a pressure in the second vacuum container; and

20 heating means for allowing the dyestuff to penetrate/disperse into the molded resin article, after the dyestuff sublimes and a vapor of the dyestuff is deposited on the surface of the molded resin article.

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~~24. The coloring apparatus for the resin surface layer according to any one of claims 21, 22 and 23 which further contains:~~

25 ~~a stirring mechanism for stirring the molded resin article of a powder form.~~

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25. The coloring apparatus for the resin surface layer according to any one of claims 21, 22 and 23 which further contains:

a wind-up mechanism for winding up the molded resin article of a form selected from a textile form, a fiber form and a film form around a reception side reel from a supply side reel under reduced pressure.

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26. A molded resin article wherein its surface layer is modified by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12.

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27. A molded resin article wherein its surface layer is modified by the modification method of the resin surface layer according to claim 13.

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28. A molded resin article wherein its surface layer is modified by the modification method of the resin surface layer according to claim 14.

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29. A molded resin article wherein its surface layer is modified by the modification method of the resin surface layer according to claim 15.

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30. A plastic lens wherein its surface layer is modified by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.

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31. A plastic lens wherein its surface layer is modified by the modification method of the resin surface layer according to claim 14.

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32. A resin coat lens wherein its resin surface layer is modified by

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~~the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.~~

5 33. A resin coat lens wherein its resin surface layer is colored by the coloring method of the resin surface layer according to claim 14.

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~~34. A plastic film wherein its surface layer is modified by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.~~

10 35. A plastic film wherein its surface layer is modified by the modification method of the resin surface layer according to claim 14.

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~~36. A fiber wherein its surface layer is modified by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.~~

15 37. A fiber wherein its surface layer is modified by the modification method of the resin surface layer according to claim 14.

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~~38. A plastic optical fiber wherein its surface layer is modified by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.~~

20 39. A plastic optical fiber wherein its surface layer is colored by the coloring method of the resin surface layer according to claim 14.

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40. A molded resin article wherein its surface layer is modified with a fluorescent dyestuff having sublimation properties and an affinity for a resin of the molded resin article to be coated, by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to impart a fluorescent light emitting function to the surface layer.

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10. A molded resin article wherein its surface layer is modified with a photochromic dyestuff having sublimation properties and an affinity for a resin of the molded resin article to be coated, by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to impart a photochromic function to the surface layer.

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15. A molded resin article wherein its surface layer is modified with an organic metal compound having sublimation properties and an affinity for a resin of the molded resin article to be coated, by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to impart an X ray and/or electron ray and/or ray absorption function to the surface layer.

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20. A molded resin article wherein its surface layer is modified with an antibacterial or antifungal agent having sublimation properties and an affinity for a resin of the molded resin article to be coated, by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to impart an antibacterial or antifungal function to the surface layer.

44. A molded resin article wherein its surface layer is modified

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~~with a medicinal activity organic compound having sublimation properties and an affinity for a resin of the molded resin article to be coated, by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to impart a medicinal activity function to the surface layer.~~

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45. A molded resin article wherein its surface layer is modified with an organic compound having sublimation properties and an affinity for a resin of the molded resin article to be coated, and assuming a physiological activity to an animal/plant, by the modification method of the resin surface layer according to any one of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to impart a function as an agricultural chemical to a surface layer.

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